



# Effect of ozonation pretreatment on the surface properties and catalytic activity of multi-walled carbon nanotube

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## ABSTRACT

Multi-walled carbon nanotube (MWCNT) has been used in the catalytic ozonation of oxalic acid in aqueous solution, which was pretreated using ozone and was characterized by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), nitrogen adsorption and Boehm titration. The effect of ozonation pretreatment on the catalytic activity of MWCNT and the ozonation mechanism of oxalic acid in the presence of MWCNT were investigated. The results indicate that with the increasing pretreatment time, the atom ratio of oxygen to carbon and the number of surface acid groups on MWCNT increase, while the catalytic activity of MWCNT on ozonation of oxalic acid decreases, suggesting that the chemical characteristics of MWCNT mainly determine its catalytic activity on oxalic acid mineralization. The inhibition of *tert*-butyl alcohol on the degradation of oxalic acid is slight for pristine MWCNT catalytic ozonation and this inhibition trend becomes more obvious when MWCNT was pretreated by ozone. A free radical mechanism was proposed which involves both surface reactions and bulk reactions between the oxalic acid and active species.

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## 1. Introduction

Since the discovery of multi-walled carbon nanotube (MWCNT) by Iijima, a lot of attention has been paid to its synthesis, characterization, modification and application [1]. As is well known, MWCNT has some good characters: (1) the high mesoporous area without the existence of microporous, and the mesoporous is in favor of reactants diffusion on catalyst surface compared with the microporous in aqueous solution [2]; (2) the resistance to abrasion and acidic/basic environments makes them suitable for severe reaction conditions [3,4]. These advantages of MWCNT make it an ideal candidate to use as catalyst or catalyst support in heterogeneous catalysis. Actually, MWCNT has been widely used as catalyst support for catalytic oxidation in aqueous solution for environmental protection [2,5–8], while the direct use of MWCNT as catalyst was seldom reported [4].

Although MWCNT is more resistant to ozonation compared with activated carbon [8], the generations of some functional

groups on CNT surface are observed after its pretreatment with ozone in either gas phase [9,10] or aqueous solution [11], which are beneficial to the dispersion of CNT in composite [10] or water [11]. Furthermore, it is reported that the MWCNT pretreated with  $\text{HNO}_3\text{--H}_2\text{SO}_4$  mixture exhibits a higher activity than pristine MWCNT in the wet air oxidation of phenol due to the generation of functional groups (mainly carboxyl acid group) on its surface [4]. It can be expected that some functional groups would be generated gradually on the MWCNT surface if it is employed as catalyst in ozonation, which would lead to some change on its catalytic activity. However, there is no report regarding the effect of MWCNT surface modification on its activity in heterogeneous catalytic ozonation.

It is well known that oxalic acid is refractory to ozonation with a reaction rate  $k_{\text{O}_3}$  lower than  $0.04\text{ M}^{-1}\text{ s}^{-1}$  [12], and is often observed as one of the most common by-products in ozonation of many refractory organic compounds [13,14]. Therefore, oxalic acid was always employed as a target pollutant to examine the activity of catalysts in heterogeneous catalytic ozonation [15–17]. In this study, the effect of ozonation pretreatment on the surface properties of MWCNT was investigated, and its effect on catalytic activity of MWCNT was evaluated using oxalic acid as a target compound. The relation between surface properties and catalytic activity of MWCNT was also discussed.

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## 2. Materials and methods

### 2.1. Materials and reagents

Commercial Aligned-MWCNT (i.d.: 10–20 nm, length: 5–15  $\mu\text{m}$ , purity: >95%) was obtained from Shenzhen Nanotech. Port. Co. Ltd. (Shenzhen, China). All the reagents used for the experiment were of analytical grade. Distilled water was used for all the experiments except for the case of ozonation in the presence of MWCNT with different ozonation time in the absence of oxalic acid under the condition of pH 3.0, in which ultrapure water (Millipore Q Biocel system) was used for total organic carbon (TOC) analysis.

### 2.2. MWCNT pretreatment

Ozonation pretreatment was performed in a conical flask by treating MWCNT (2 g) with an ozone flow rate of  $40 \text{ mg min}^{-1}$  (oxygen flow rate was  $1 \text{ L min}^{-1}$ ) at room temperature. Ozone was produced from pure oxygen in a DHX-SS-1G ozone generator (Harbin Jiujiu Electric Chemical Engineering Ltd., China) and fed into the conical flask for different periods (10, 30, 60 and 120 min). After each treatment, the MWCNT was dried overnight in an oven at 393 K.

### 2.3. Ozonation and catalytic ozonation procedure

Ozonation and catalytic ozonation were carried out in semi-batch mode. Ozone was continuously bubbled into a 1.0 L aqueous solution of oxalic acid (1 mM) through a porous porcelain pellet. In the catalytic ozonation experiment, ozone was introduced into the reactor immediately after the MWCNT catalyst ( $100 \text{ mg L}^{-1}$ ) was dosed into the solution, which corresponds to the beginning of the reaction. Ozone flow rate was  $20 \text{ mg min}^{-1}$  when oxygen flow rate was controlled at  $480 \text{ mL min}^{-1}$  and reaction temperature was controlled at  $293 \pm 1 \text{ K}$ . The initial pH value of the oxalic acid solution was 3.0 without any adjustment. During the experiments of ozonation of MWCNT with different ozonation time in the absence of oxalic acid, pH values were adjusted to 3.0 using concentrated  $\text{HNO}_3$  and NaOH solutions.

### 2.4. Characterization of MWCNT

X-ray photoelectron spectroscopy (XPS) was used to quantify the oxidation of MWCNT surface using a PHI 5700 multi-ESCA system. Fourier transform infrared spectroscopy (FTIR) was used to identify the functional groups on MWCNT surface using a Bruker Fourier transform spectrophotometer Magna-IR 750. The texture of MWCNT was characterized by the adsorption of nitrogen at 77 K on a Micromeritics ASAP 2020 system using the Brunauer–Emmett–Teller (BET) method. The point of zero charge (PZC) of MWCNT was estimated a method [8] similar to a modified version [18] of the mass titration method [19]. The numbers of acidic and basic groups on MWCNT were examined using Boehm titration [20].

### 2.5. Analysis methods

The concentration variation of oxalic acid was analyzed by a high performance liquid chromatograph (HPLC) equipped with an automatic Waters 717 plus autosampler injector and a Waters 1525 binary pump, using a Atlantis dC<sub>18</sub> column ( $5 \mu\text{m} \times 4.6 \text{ mm} \times 250 \text{ mm}$ ) and acetonitrile/water (20/80 in v/v) as the mobile phase (phosphoric acid was used to keep the water pH at 2.5) with a rate of  $1 \text{ mL min}^{-1}$ . The water sample was detected by a UV detector (Waters 2487 dual  $\lambda$  absorbance detector) at 210 nm. The

concentration of hydrogen peroxide in aqueous solution was determined by a photometric method [21].

During the experiments of ozonation of MWCNT with different ozonation time in the absence of oxalic acid, TOC was analyzed by a TOC Analyzer (Analytik Jena Multi N/C 3100). To evaluate the effect of *tert*-butyl alcohol (TBA) on oxalic acid adsorption on MWCNT, the concentration of TBA was also determined by TOC analysis. Because the samples were filtered by a membrane with  $0.2 \mu\text{m}$  pore size before TOC analysis, the TOC values actually correspond to the dissolved TOC.

## 3. Results and discussion

### 3.1. Characterization of MWCNT with ozonation pretreatment

The variations in the surface mass of carbon and oxygen atoms, as well as the oxygen to carbon (O/C) ratio with different ozonation pretreatment time are summarized in Fig. 1. The surface oxygen atom increases rapidly from 2.28% of pristine MWCNT to 4.94% within the initial pretreatment time 10 min, and then slows down until the surface oxygen atom of MWCNT eventually reaches a plateau of 6.51% at ozonation pretreatment time of 120 min. This phenomenon coincides with the previous study, indicating that the surface oxygen atom increases from 0.71% to 5.30% after 60 min treatment of MWCNT with UV/ozone [10]. In addition, a similar trend was also observed in Fig. 1 for the variation of O/C ratio with respect to ozonation pretreatment time.

As is well known, ozonation of activated carbon would release soluble organics into bulk water that lead to the increase of TOC [22]. Furthermore, it is observed that the TOC derived from ozone attack on the activated carbons, which were pretreated by gas ozone for 10 and 120 min, were increased during the first 30 min of ozonation in the absence of organic [23]. In the present study, ozonation of MWCNT in the absence of oxalic acid was conducted to evaluate the effect of ozonation pretreatment on TOC release, and the results are presented in Fig. 2. It is obvious that the TOC increases with reaction time during ozonation of MWCNT with pretreatment or not. Furthermore, the TOC release in the ozonation of MWCNT increases with the prolonging of ozonation pretreatment time. As shown in Fig. 1, the surface mass of C atoms decreases with the increasing of ozonation pretreatment time, it is speculated that these C atoms on MWCNT after ozonation pretreatment can be easier to release into bulk water than that of pristine MWCNT during ozonation in aqueous solution, then results in a higher release of TOC.

Based on the reduction phenomenon of increase rate in O/C ratio on MWCNT after 10 min pretreatment in Fig. 1, the

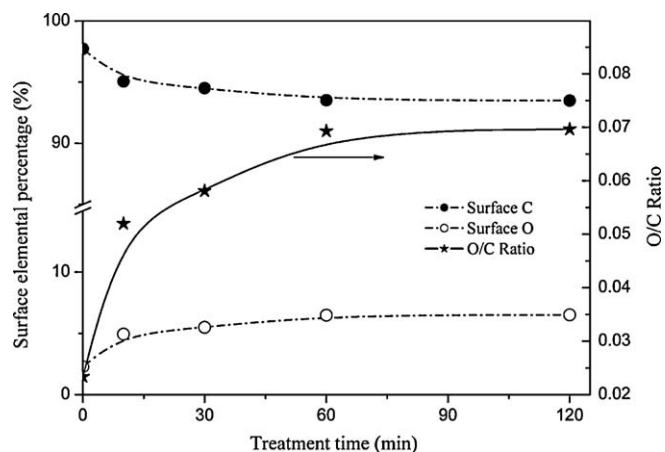
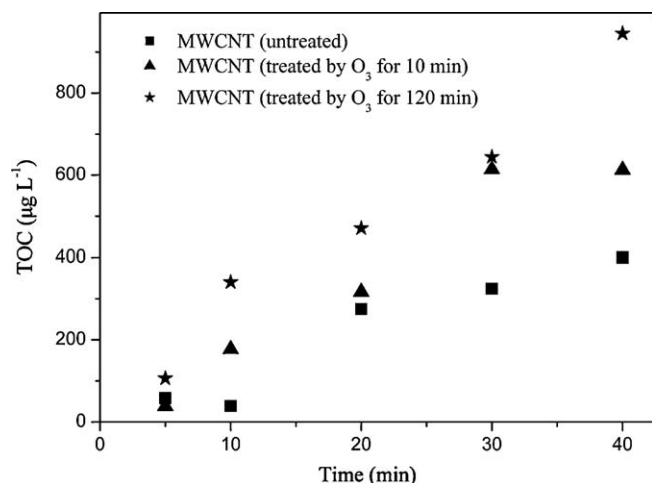
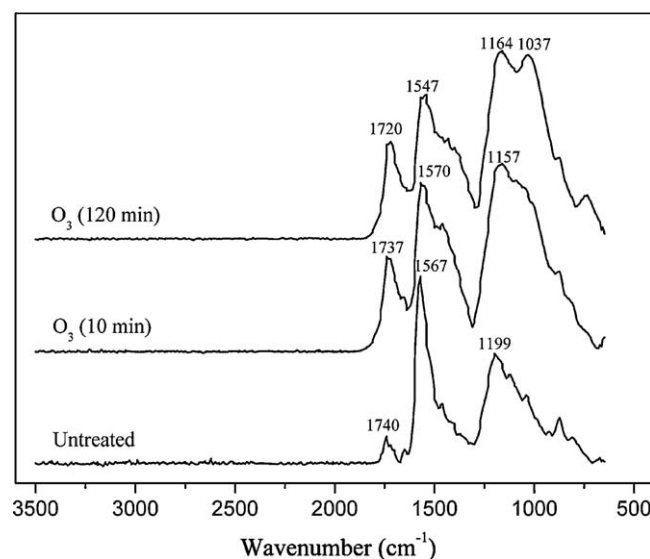


Fig. 1. Surface atomic percentage of carbon, oxygen and O/C atomic ratio of MWCNT with different ozonation time.



**Fig. 2.** Evolution of TOC during the ozonation of MWCNT in water in the absence of organics (reaction conditions:  $T = 293\text{ K}$ ; initial pH 3.0; gas flow rate =  $480\text{ mL min}^{-1}$ ; ozone gas concentration =  $20\text{ mg min}^{-1}$ ; catalyst dose =  $100\text{ mg L}^{-1}$ ).



**Fig. 3.** FTIR spectra of the MWCNT with different ozonation time.

comparative experiments were carried out to investigate the characterization conversion of the MWCNT surface with ozonation pretreatment time, and the FTIR spectra of MWCNT in the range  $700\text{--}3500\text{ cm}^{-1}$  are shown in Fig. 3.

As shown in Fig. 3, three peaks are detected at 1199, 1567 and  $1740\text{ cm}^{-1}$  for pristine MWCNT. It is generally believed that the peaks at 1740 and  $1567\text{ cm}^{-1}$  correspond to C=O stretching mode in the carboxyl acid group and the C=C stretching mode of nanotube [4,9,10,24]. Furthermore, as observed in the previous studies [9,24], the peak around  $1200\text{ cm}^{-1}$  is attributed to the C–O stretching mode in the ester groups [9].

From Fig. 3, it also can be seen that the intensity of the peak at  $1740\text{ cm}^{-1}$  increases significantly after 10 min of ozonation pretreatment, meaning that the number of carboxyl acid groups on the surface of pretreated MWCNT increases. Additionally, a notable blue shift of this peak appears when the pretreatment time is further increased from 10 to 120 min. A similar phenomenon was observed in the acid treatment of single-walled CNT with  $\text{H}_2\text{SO}_4\text{--HNO}_3$  mixture, suggesting that the formation of hydrogen bonds between the carboxyl acid groups would be more effective due to the increase in carboxyl acid groups with pretreatment time, and this lowers the frequency of the C=O stretching mode [24]. Fig. 3 also shows that the intensity decreases for the peak at  $1567\text{ cm}^{-1}$  as the ozonation pretreatment time is prolonged, while the opposite trend is observed for the peak at  $1199\text{ cm}^{-1}$ . Additionally, the peak at  $1199\text{ cm}^{-1}$  of pristine MWCNT splits into two peaks at 1164 and  $1037\text{ cm}^{-1}$  after 120 min ozonation pretreatment, and the peak at  $1037\text{ cm}^{-1}$  is assigned to the C–C–O stretching mode in unsaturated hydroxyl groups [25]. This result illustrates that the C=C double bond is attacked by ozone and then transforms to a hydroxyl group, which can be further oxidized to carbonyl and carboxyl acid groups concurrently [11], leading to a reduction of intensity of the peak at  $1567\text{ cm}^{-1}$  and an increase in

intensities of other peaks during ozonation pretreatment compared to the case of pristine MWCNT.

Boehm titration was performed to obtain more detailed information about the functional groups on the MWCNT surface after ozonation pretreatment, and the results are shown in Table 1. It can be found that the  $\text{pH}_{\text{PZC}}$  of MWCNT decreases with the increasing ozonation pretreatment time, which should be mainly attributed to the elimination of basic groups and the increasing acid groups on MWCNT surface. The number of acid groups increases remarkably within the initial 10 min, which is in accordance with the variation trend of O/C ratio (Fig. 1). Furthermore, a slight increase in surface area ( $S_{\text{BET}}$ ) and  $V_{\text{meso}}$  is respectively determined after ozonation pretreatment (Table 1).

### 3.2. Catalytic activity of MWCNT with ozonation pretreatment

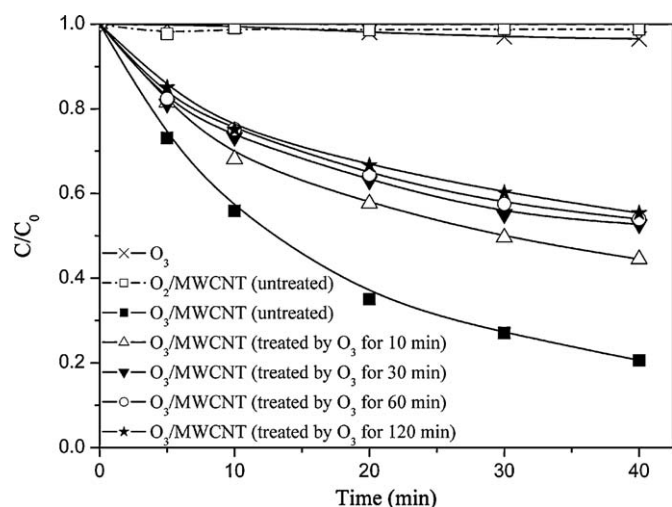
#### 3.2.1. Ozonation of oxalic acid in the presence of MWCNT with ozonation pretreatment

Fig. 4 shows the results of the catalytic ozonation of oxalic acid in aqueous solution by MWCNT with or without ozonation pretreatment. The results indicate that ozonation alone or adsorption on MWCNT only results in the less than 4.0% removal of oxalic acid after 40 min, namely ozonation alone and adsorption scarcely contribute to the elimination of oxalic acid compared to the case of catalytic ozonation and can therefore be neglected. In Fig. 4, it is obvious that the catalytic activity of MWCNT decreases with the increasing ozonation pretreatment time. The activity of MWCNT remarkably reduces within the initial 10 min pretreatment, and it becomes insignificant with the increase of ozonation pretreatment time. This phenomenon is similar to the variation trends of the O/C ratio and the surface groups of treated MWCNT (Fig. 1 and Table 1).

**Table 1**

Texture and chemical characteristics of MWCNT with and without ozonation pretreatment.

Sample	$S_{\text{BET}}$ ( $\text{m}^2\text{ g}^{-1}$ )	$V_{\text{meso}}$ ( $\text{cm}^3\text{ g}^{-1}$ )	Acidity ( $\mu\text{mol g}^{-1}$ )			Basicity ( $\mu\text{mol g}^{-1}$ )	$\text{pH}_{\text{PZC}}$
			Carboxyl	Lactone	Phenol		
Untreated	117.5	0.53	70	14	37	163	6.1
$\text{O}_3$ (10 min)	125.1	0.56	196	67	39	70	3.9
$\text{O}_3$ (120 min)	129.2	0.57	238	98	61	29	3.6



**Fig. 4.** Effect of ozonation pretreatment on the activity of MWCNT for ozonation of oxalic acid (reaction conditions:  $T = 293\text{ K}$ ; initial pH 3.0; initial concentration of oxalic acid =  $1\text{ mM}$ ; gas flow rate =  $480\text{ mL min}^{-1}$ ; ozone gas concentration =  $20\text{ mg min}^{-1}$ ; catalyst dose =  $100\text{ mg L}^{-1}$ ).

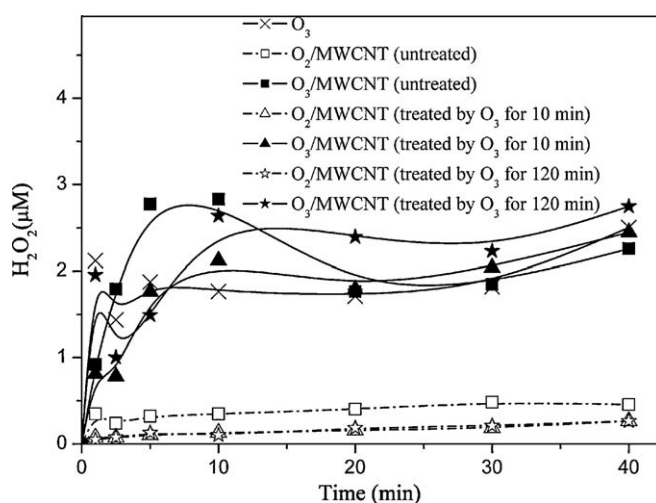
Based on the experimental results and the analysis mentioned above, it is suggested that the activity loss of MWCNT after ozonation pretreatment is mainly attributed to the increase of acidic groups and the reduction of its basic character. These results agree with the previous findings in the effect investigation of preozonation treatment of activated carbon on its catalytic activity for ozonation of 1,3,6-naphthalenetrisulphonic acid [23].

### 3.2.2. Evolution of hydrogen peroxide concentrations during ozonation of oxalic acid in the presence of MWCNT with ozonation pretreatment

It is reported that a certain concentration of hydrogen peroxide was detected in the processes of ozone decomposition either under acidic condition [26,27] or in the presence of activated carbon catalyst [28], and degradation of organic pollutant by carbon catalytic ozonation [8,29,30]. Additionally, it is found that a small amount of hydrogen peroxide formed through the reduction of oxygen (Eq. (1)) by the basic groups of carbon materials [31,32]. Therefore, the variations of hydrogen peroxide concentration versus reaction time were investigated in the processes of ozonation alone, MWCNT adsorption and MWCNT catalytic ozonation for the degradation of oxalic acid in aqueous solution.



As shown in Fig. 5, hydrogen peroxide is yielded during the MWCNT adsorption in the presence of oxygen. Furthermore, the amount of hydrogen peroxide in the presence of pristine MWCNT is higher compared with the case of MWCNT after ozonation pretreatment, which should be caused by the decrease of redox capacity of pretreated MWCNT due to its less amount of basic groups after ozonation pretreatment (Table 1). Certain concentrations of hydrogen peroxide are generated as a result of ozone decomposition in the processes of ozonation alone and MWCNT catalytic ozonation. The concentration of hydrogen peroxide varies with reaction time, indicating that hydrogen peroxide should participate in the process of oxalic acid degradation and might be an important intermediate in catalytic ozonation. Beltrán et al. observed that, at a given time, the concentration of hydrogen peroxide generated in the presence of activated carbon is lower than that in its absence during the ozonation of either gallic acid [29] or diclofenac [30], and suggested that the lower hydrogen

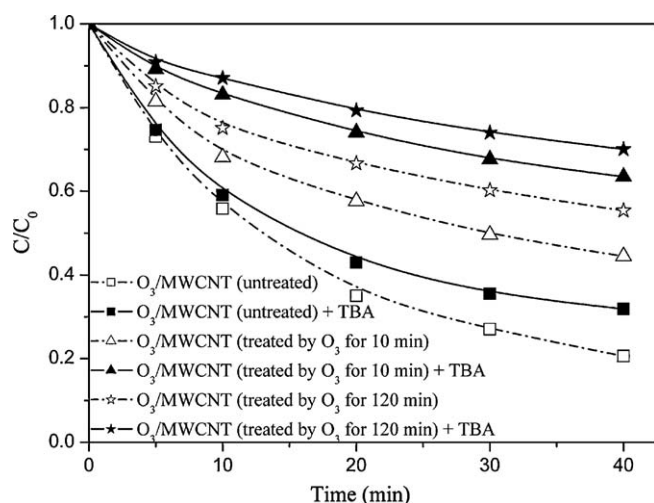


**Fig. 5.** Evolution of hydrogen peroxide concentration during ozonation alone and catalytic ozonation in the presence of MWCNT for the degradation of oxalic acid (reaction conditions:  $T = 293\text{ K}$ ; initial pH 3.0; initial concentration of oxalic acid =  $1\text{ mM}$ ; gas flow rate =  $480\text{ mL min}^{-1}$ ; ozone gas concentration =  $20\text{ mg min}^{-1}$ ; catalyst dose =  $100\text{ mg L}^{-1}$ ).

peroxide generation during the ozone-activated carbon process is undoubtedly due to its reactivity with the activated carbon surface where it likely reacts with adsorbed ozone to yield hydroxyl radicals [33]. In the present study, no direct correlation between hydrogen peroxide evolution and catalytic activity of MWCNT with or without ozonation pretreatment is established. However, detailed investigations on the relationship between the surface properties of activated carbon and its activity on the decomposition of hydrogen peroxide were carried out by Huang et al. [34] and Oliveira et al. [35], who suggested that the activity decreases with the number increase of surface acidic groups after activated carbon pretreatment by concentrated  $\text{HNO}_3$  [34] and increases with the number increase of basic groups after activated carbon calcination under hydrogen atmosphere [35]. It is obvious that the decomposition of hydrogen peroxide by MWCNT would be suppressed after ozonation pretreatment due to its basic groups decrease and acidic groups increase, which would be unfavorable to yield free radical species and retard the removal of oxalic acid.

### 3.2.3. Effect of the presence of TBA on the catalytic activity of MWCNT with ozonation pretreatment

As a well known hydroxyl radical ( $\cdot\text{OH}$ ) scavenger, TBA has been widely used as a probe to investigate the role of  $\cdot\text{OH}$  in oxalic acid removal by activated carbon catalytic ozonation [15,17]. The effects of TBA on oxalic acid degradation by ozonation in the presence of MWCNT with or without ozonation pretreatment were investigated, and the results are presented in Fig. 6. It is found that the presence of TBA decreases the degradation efficiency of oxalic acid comparatively in the presence of MWCNT with or without ozonation pretreatment. However, this inhibition may also be caused by the adsorption of TBA on the MWCNT surface. It could be imagined that the oxidation of oxalic acid would be retarded if most active sites on the MWCNT surface are occupied due to the adsorption of TBA. Thus, a series of adsorption experiments was carried out to investigate the TBA adsorption on the MWCNT surface and the possible effect of TBA on oxalic acid adsorption on the MWCNT surface, as shown in Fig. 7. It is observed that the differences for the oxalic acid adsorption are inconspicuous with or without TBA, and the amount of TBA adsorption is no more than 2%. Similar results were obtained by Beltrán et al. [15], who reported that the addition of TBA has no effect on the adsorption of oxalic acid and TBA scarcely adsorbs on the surface of activated carbon



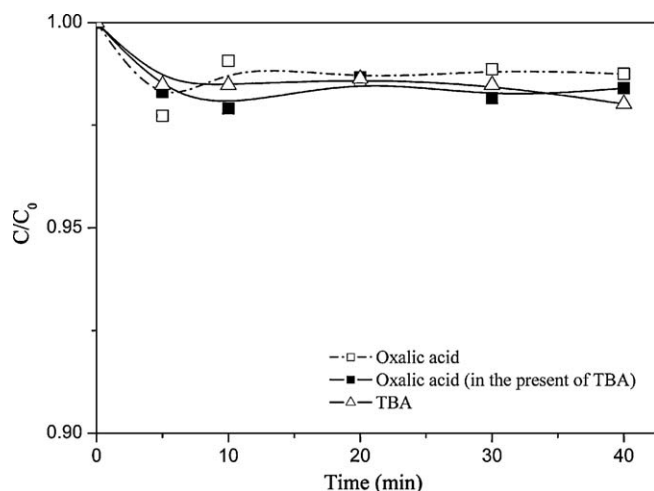
**Fig. 6.** Effect of TBA on the ozonation of oxalic acid in the presence of MWCNT catalyst (reaction conditions:  $T = 293\text{ K}$ ; initial pH 3.0; initial concentration of oxalic acid =  $1\text{ mM}$ ; gas flow rate =  $480\text{ mL min}^{-1}$ ; ozone gas concentration =  $20\text{ mg min}^{-1}$ ; catalyst dose =  $100\text{ mg L}^{-1}$ ; TBA concentration =  $1\text{ mM}$ ).

during the ozonation of oxalic acid with activated carbon at pH 2.5. Based on the above experimental results and analysis, it can be deduced that  $\cdot\text{OH}$  should participate in the oxalic acid removal by MWCNT catalytic ozonation.

Additionally, Fig. 6 reveals that the inhibitions of TBA on the catalytic activity of MWCNT after ozonation pretreatment are more significantly compared with that of pristine MWCNT, which should be caused by the change on surface properties of MWCNT after ozonation pretreatment and the detailed analysis will be presented later.

### 3.3. Considerations on the reaction mechanism

As described in our previous study, it is argued that MWCNT catalytic ozonation should have a mechanism similar to that of activated carbon since MWCNT and activated carbon have many similarities from either the bonding and structure or the obtained experimental results [8]. As far as the degradation of oxalic acid by activated carbon catalytic ozonation is concerned, both Beltrán et al. [15] and Faria et al. [17] have proposed that this process



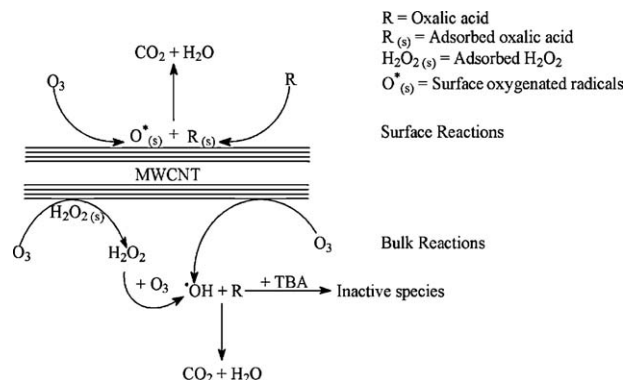
**Fig. 7.** Effect of TBA on oxalic acid adsorption on MWCNT (reaction conditions:  $T = 293\text{ K}$ ; initial pH 3.0; initial concentration of oxalic acid =  $1\text{ mM}$ ; oxygen gas flow rate =  $480\text{ mL min}^{-1}$ ; catalyst dose =  $100\text{ mg L}^{-1}$ ; TBA concentration =  $1\text{ mM}$ ).

follows a free radical mechanism. However, it is still in debate where the reaction between active species and oxalic acid mainly takes place. Either in the bulk solution [15] or on the surface of activated carbon [17] has been proposed since a significant inhibition on oxalic acid removal in the presence of TBA was observed by Beltrán et al. [15] whereas no affection was found by Faria et al. [17] when the initial pH of solution is no more than 3.0. In the present study, the oxidation of oxalic acid by  $\cdot\text{OH}$  in bulk solution could be completely inhibited because almost all of the TBA remains in bulk solution (Fig. 7). However, the TBA could hardly affect the oxidation of oxalic acid by  $\cdot\text{OH}$  if the reaction occurred on the surface of MWCNT. The results in Fig. 6 have confirmed a considerable removal of oxalic acid even in the presence of TBA. Based on the results and analysis aforementioned, it is suggested that the ozonation of oxalic acid occurs through a free radical mechanism involving both surface reactions and bulk reactions between the oxalic acid and active species. A similar approach is proposed previously by Faria et al. [17] for ozonation of oxalic acid in the presence of activated carbon.

The main possible reaction pathways of MWCNT catalytic ozonation for the degradation of oxalic acid in aqueous solution are presented in Fig. 8. It must be pointed out that the active species of  $\text{O}_2^{\cdot-}$  in surface reactions represent any oxygen-containing active species (such as  $\cdot\text{OH}$ ) on the MWCNT surface, and whether  $\cdot\text{OH}$  is the main active species or not still could not be confirmed by experimental evidence due to the complex of surface reactions.

As for reactions in bulk solution, the free radical species for the oxidation of oxalic acid can be generated by two ways. One is assume that MWCNT acts as an initiator in the transformation process of ozone into active species (such as  $\cdot\text{OH}$ ) in solution [17,36]; another possibility is that ozone reacts with some surface groups of MWCNT to generate adsorbed hydrogen peroxide, then hydrogen peroxide diffuse into bulk solution and reacts with ozone to yield  $\cdot\text{OH}$ . In the case of reactions on the surface of MWCNT, it is suggested that ozone adsorbs and decomposes on the surface of MWCNT to form surface active species ( $\text{O}_2^{\cdot-}$ ), which can oxidize the adsorbed oxalic acid to carbon dioxide and water.

As aforementioned, MWCNT pretreated by ozone leads to the increase of acidic groups and the reduction of its basic character (Table 1), which affects ozonation of oxalic acid in two aspects. The first one is disadvantageous to transfer ozone and some intermediates (such as hydrogen peroxide) into high active species. The decrease of basic groups and the increase of acidic groups on activated carbon surface lead to the decrease of the activity on transformation ozone in aqueous solution into  $\cdot\text{OH}$  [28,37] and on the decomposition of hydrogen peroxide [34,35]. It is suggested that an activated carbon catalyst with a higher activity on the decomposition of hydrogen peroxide usually has a higher



**Fig. 8.** Scheme of the mainly reaction pathways of MWCNT catalytic ozonation for the degradation of oxalic acid in aqueous solution.

activity on either the decomposition of ozone [28] or the ozonation of organic pollutants [29,30]. In the present study, it is deduced that MWCNT pretreated by ozone is disadvantageous to the decomposition of ozone or hydrogen peroxide and the formation of high active species. Thus, it would lead to a decrease on catalytic activity of MWCNT in either surface reactions or bulk reactions and lower the degradation efficiency of oxalic acid.

Another possible effect is the adsorption of oxalic acid on MWCNT surface. The processes of surface reactions include adsorptions of ozone and oxalic acid, surface reaction and desorption. It is obvious that the surface properties of MWCNT have a significant effect on the adsorption of oxalic acid (or its corresponding anions) on its surface. It is well known that the surface of carbon is positively charged at the pH of solution below the  $\text{pH}_{\text{PZC}}$  of carbon [38]. In the present study, the surface of pristine MWCNT should be positively charged since the  $\text{pH}_{\text{PZC}}$  of pristine MWCNT is 6.1 and the pH of solution varies in the range of 3.0–3.6 during the process of catalytic ozonation. Therefore, the adsorption of anion species of oxalic acid ( $\text{pK}_{\text{a}1} = 1.23$ ;  $\text{pK}_{\text{a}2} = 4.19$ ) on pristine MWCNT surface would be favored. As for MWCNT after ozonation pretreatment, its  $\text{pH}_{\text{PZC}}$  quickly decreases from 6.1 to 3.9 after 10 min pretreatment (Table 1). According to the view of Nawrocki et al. [39], the surface of metal oxide has obvious positive charge only when the absolute value of the difference between  $\text{pH}_{\text{PZC}}$  of metal oxide and pH of solution is more than two units. Hence, it is reasonable that the positive charge on the surface of MWCNT would be largely reduced after ozonation pretreatment. Therefore, the adsorption of anion species of oxalic acid on MWCNT surface would be decreased. Actually, the basic activated carbons present better adsorption capacities than more acidic ones when oxalic acid solutions are existed either in the molecular or anionic form, which has been proved in the adsorption experiments by Faria et al. [17]. It is argued that the decreases of oxalic acid adsorption on the MWCNT surface will weaken the function of surface reactions during the process of oxalic acid removal. In other words, the contribution of bulk reactions between  $\cdot\text{OH}$  and oxalic acid (or its corresponding anions) to the degradation of oxalic acid would be strengthened, then it is not surprising that the addition of TBA has a more significant inhibition on the activity of MWCNT after ozonation pretreatment compared with that of pristine MWCNT (Fig. 6).

#### 4. Conclusions

The chemical composition of the MWCNT surface is changed with ozonation pretreatment. As the exposure time of MWCNT to ozone gas prolonged, the number of basic groups decreases and the number of acidic groups increases on the MWCNT surface, especially for carboxyl acid group, leading to the decreases of both the  $\text{pH}_{\text{PZC}}$  of MWCNT and the activity on oxalic acid removal by MWCNT catalytic ozonation.

Hydrogen peroxide is generated and participated in the process of oxalic acid ozonation in the presence of MWCNT with or without ozonation pretreatment. The mechanism of MWCNT catalytic ozonation was proposed to be similar to that of activated carbon. It is suggested that the ozonation of oxalic acid in the presence of

MWCNT occurs both on the MWCNT surface and in the bulk solution.

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#### References

- [1] P. Serp, M. Corrias, P. Kalck, *Appl. Catal. A: Gen.* 253 (2003) 337–358.
- [2] G. Ovejero, J.L. Sotelo, M.D. Romero, A. Rodríguez, M.A. Ocaña, G. Rodríguez, J. García, *Ind. Eng. Chem. Res.* 45 (2006) 2206–2212.
- [3] Z.H. Kang, E.B. Wang, B.D. Mao, Z.M. Su, L. Gao, L. Niu, H.Y. Shan, L. Xu, *Appl. Catal. A: Gen.* 299 (2006) 212–217.
- [4] S. Yang, X. Li, W. Zhu, J. Wang, C. Descorme, *Carbon* 46 (2008) 445–452.
- [5] J. García, H.T. Gomes, P. Serp, P. Kalck, J.L. Figueiredo, J.L. Faria, *Carbon* 44 (2006) 2384–2391.
- [6] C. Cui, X. Quan, H. Yu, Y. Han, *Appl. Catal. B: Environ.* 80 (2008) 122–128.
- [7] B. Gao, G.Z. Chen, G.L. Puma, *Appl. Catal. B: Environ.* 89 (2009) 503–509.
- [8] Z.Q. Liu, J. Ma, Y.H. Cui, *Carbon* 44 (2008) 890–897.
- [9] D.B. Mawhinney, V. Naumenko, A. Kuznetsova, J.T. Yates, J. Liu, R.E. Smalley, *J. Am. Chem. Soc.* 122 (2000) 2383–2384.
- [10] M.L. Sham, J.K. Kim, *Carbon* 44 (2006) 768–777.
- [11] M. Li, M. Boggs, T.P. Beebe, C.P. Huang, *Carbon* 46 (2008) 466–475.
- [12] J. Hoigné, H. Bader, *Water Res.* 17 (1983) 185–194.
- [13] M. Carbajo, F.J. Beltrán, O. Gimeno, B. Acedo, F.J. Rivas, *Appl. Catal. B: Environ.* 74 (2007) 203–210.
- [14] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, *Appl. Catal. B: Environ.* 83 (2008) 150–159.
- [15] F.J. Beltrán, F.J. Rivas, L.A. Fernández, P.M. Álvarez, R. Montero-de-Espinosa, *Ind. Eng. Chem. Res.* 41 (2002) 6510–6517.
- [16] D.S. Pines, D.A. Reckhow, *Environ. Sci. Technol.* 36 (2002) 4046–4051.
- [17] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, *Appl. Catal. B: Environ.* 79 (2008) 237–243.
- [18] J.A. Menéndez, J. Phillips, B. Xia, L.R. Radovic, *Langmuir* 12 (1996) 4404–4410.
- [19] J.S. Noh, J.A. Schwarz, *Carbon* 28 (1990) 675–682.
- [20] H.P. Boehm, *Carbon* 32 (1994) 759–769.
- [21] H. Bader, V. Sturzenegger, J. Hoigné, *Water Res.* 22 (1988) 1109–1115.
- [22] J. Rivera-Utrilla, M. Sánchez-Polo, *Appl. Catal. B: Environ.* 39 (2002) 319–329.
- [23] M. Sánchez-Polo, J. Rivera-Utrilla, *Carbon* 41 (2003) 303–307.
- [24] J. Zhang, H. Zou, Q. Qing, Y. Yang, Q. Li, Z. Liu, X. Guo, Z. Du, *J. Phys. Chem. B* 107 (2003) 3712–3718.
- [25] U.J. Kim, C.A. Furtado, X. Liu, G. Chen, P.C. Eklund, *J. Am. Chem. Soc.* 127 (2005) 15437–15445.
- [26] K. Sehested, H. Corfitzen, J. Holcman, E.J. Hart, *J. Phys. Chem. A* 102 (1998) 2667–2672.
- [27] I. Fábjan, *Pure Appl. Chem.* 78 (2006) 1559–1570.
- [28] P.M. Álvarez, J.F. García-Araya, F.J. Beltrán, I. Giráldez, J. Jaramillo, V. Gómez-Serrano, *Carbon* 44 (2006) 3102–3112.
- [29] F.J. Beltrán, J.F. García-Araya, I. Giráldez, *Appl. Catal. B: Environ.* 63 (2006) 249–259.
- [30] F.J. Beltrán, P. Pocostales, P. Alvarez, A. Oropesa, J. Hazard. Mater. 163 (2009) 768–776.
- [31] C.A. Leon y Leon, J.M. Solar, V. Calemme, L.R. Radovic, *Carbon* 30 (1992) 797–811.
- [32] E. Ahumada, H. Lizama, F. Orellana, C. Suárez, A. Huidobro, A. Sepúlveda-Escribanos, F. Rodríguez-Reinos, *Carbon* 40 (2002) 2827–2834.
- [33] F.J. Beltrán, I. González, J.F. García-Araya, *Ind. Eng. Chem. Res.* 47 (2008) 1058–1065.
- [34] H.H. Huang, M.C. Lu, J.N. Chen, C.T. Lee, *Chemosphere* 51 (2003) 935–943.
- [35] L.C.A. Oliveira, C.N. Silva, M.I. Yoshida, R.M. Lago, *Carbon* 42 (2004) 2279–2284.
- [36] U. Jans, J. Hoigné, *Ozone Sci. Eng.* 20 (1998) 67–90.
- [37] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, *Ind. Eng. Chem. Res.* 45 (2006) 2715–2721.
- [38] L.R. Radovic, C. Moreno-Castilla, J. Rivera-Utrilla, in: L.R. Radovic (Ed.), *Chemistry and Physics of Carbon*, Dekker, Inc., New York, 2001, pp. 227–406.
- [39] J. Nawrocki, M.P. Rigney, A. McCormick, P.W. Carr, *J. Chromatogr. A* 657 (1993) 229–282.